

PATENT SPECIFICATION

(11) 1 498 707

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(21) Application No. 17289/75 (22) Filed 25 April 1975
 (31) Convention Application No. 494 130
 (32) Filed 2 Aug. 1974 in
 (33) United States of America (US)
 (44) Complete Specification published 25 Jan. 1978
 (51) INT CL² C08C 19/28; C08F 8/00, 8/30 // C07C 39/08, 39/20,
 69/54, 93/14, 101/453; C07D 207/44

(52) Index at acceptance
 C3P D9B11 D9B1A D9D2 D9D7D1 D9D7D2 D9D8 D9E2
 C2C 1342 200 215 220 227 22Y 235 240 247 250 251 25Y
 30Y 322 32Y 351 352 360 361 362 365 366 368
 36Y 388 456 45Y 491 502 507 509 50Y 623 624
 628 630 633 635 652 658 65X 660 662 680 699
 761 763 779 793 797 79Y BZ LE LK LQ TM
 WP WS

C3E 2BX

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(54) A METHOD OF CHEMICALLY BONDING ANTIOXIDANTS INTO POLYMERIC MATERIALS

(71) We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, with offices at 1144 East Market Street, Akron, Ohio, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process for chemically bonding antioxidants into polymeric materials. More particularly this invention relates to antioxidants containing unsaturated segments and to a process of building the antioxidant into the polymeric material.

The advantages of building antioxidants into the chemical structure of polymers include the ability to resist extraction even after repeated exposure to aqueous detergent or dry-cleaning fluids. Such stabilized polymeric materials are used for carpet backing and applications where the polymer is used in solution form as in fabric treatments. These materials are also used in such applications as solvent hoses, oil seals and o-rings.

Chemically bound antioxidants have previously been incorporated in polymeric materials as a copolymerizable monomer during the polymerization stage of manufacture of the polymer. This polymerization requires the use of pure materials and specialized equipment and techniques. Network bound antioxidants have previously been prepared in natural rubber using nitrosodiphenylamine. In some cases antioxidants can also form resinous materials which are blended into the poly-

mer. These high molecular weight materials are non-migrating and are not easily extracted. 40

It is an object of the present invention to provide a method for chemically bonding antioxidants containing aliphatic unsaturation in their structures into polymeric materials. Other objects will become apparent to those skilled in this art as the description proceeds. 45

It has now been discovered that antioxidants containing aliphatic unsaturation can be chemically bonded or built into the polymer network when mechanically blended with the polymer in the presence of a free radical initiator effective to cause the unsaturated antioxidant to react with the polymer by a free radical mechanism. Thus materials which generate free radicals can be added in free form to polymeric materials mixed with the said antioxidants. 50

The preferred process comprises heating and reacting a mixture of the polymeric material and antioxidant containing aliphatic unsaturation, in the presence of a free radical initiator, for a time sufficient to cause the antioxidant to chemically bond with the polymer, the antioxidant being an acyclic compound or aryl-substituted acyclic compound. 55

The term "aliphatic unsaturation" as used herein is meant to describe unsaturation other than ring unsaturation. Thus an antioxidant containing a vinyl phenol structure has aliphatic unsaturation in the vinyl group and is effective in the present invention. A specific example of such an antioxidant is 3,5-di-t-butyl-4-vinylphenol. 70

The invention has five parameters; polymer, free radical initiator, antioxidant, time 75

and temperature. Each of the parameters can be varied to affect antioxidant-polymer chemical bonding.

Representative examples of polymers useful in the practice of the present invention are natural rubber, cis-polyisoprene, cis-polybutadiene, styrene/butadiene, acrylonitrile/butadiene, polychloroprene, ethylene/propylene, and ethylene/propylene/diene polymer. Mixtures of these polymers can be used.

Representative examples of the above-mentioned antioxidants containing aliphatic unsaturation useful in the practice of the present invention are N-(4-anilinophenyl)-methacrylamide; 3 - (3,5 - di - t - butyl-4 - hydroxyphenyl)butyl methacrylate; 3 - (3,5 - di - t - butyl - 4 - hydroxyphenyl)-propyl methacrylate; the reaction product of allyl glycidyl ether and p-aminodiphenylamine containing 3-N-(4-anilinophenyl)-amino-2-hydroxypropyl allyl ether; the reaction product of N-methylol maleimide and p-aminodiphenylamine containing N-[(4-anilinophenyl)amino methyl]maleimide, and the reaction product of glycidyl methacrylate and p-aminodiphenylamine containing 3-N-(4'-anilinophenyl)amino - 2 - hydroxypropyl methacrylate. Mixtures of such antioxidants can be used.

Free radical initiators useful in the practice of the present invention are peroxides and high energy radiation. Representative examples of free radical initiators are peroxides such as lauroyl peroxide; benzoyl peroxide; dicumyl peroxide; di-t-butyl peroxide; 2,5 - dimethyl - 2,5 - bis(2 - ethylhexanoylperoxy)hexane; acetyl peroxide; t-butyl peroxymaleic acid; t-butyl peracetate; t-butyl hydroperoxide; t-butyl-peroxypivalate; t-butyl perbenzoate; t-butyl peroctoate; 2,4-dichlorobenzoyl peroxide; 1,1-bis(t-butylperoxy) - 3,3,5 - trimethylcyclohexane; α,α' -bis(t - butylperoxy)diisopropylbenzene; 2,5-dimethyl - 2,5 - di(t - butylperoxy)hexane; 2,5 - dimethyl - 2,5 - di(t - butylperoxy)hexyne - 3; di(sec - butyl)peroxydicarbonate; 2,5 - dimethyl - 2,5 - di(hydroperoxy)hexane; cumene hydroperoxide; 1,1,3,3-tetramethylbutyl hydroperoxide; diisopropyl peroxydicarbonate; t-butyl peroxy[pivalate]; t-butyl peroxyisobutyrate; t-butyl peracetate; 1,1,3,3 - tetramethylbutyl peroxy - 2 - ethyl hexanoate; t-butylperoxy isopropyl carbonate; acetyl cyclohexylsulfonyl peroxide; isopropylbenzene dihydroperoxide; p-methane dihydroperoxide; t-butyl dihydroperoxide and t-butylperoxyisopropyl carbonate and radiation sources such as Cobalt 60. Mixtures of these free radical initiators can be used.

Concentrations of antioxidants useful in the present invention are from 0.2 part to 10 parts per 100 parts by weight of polymeric material, but from 1 part to 3 parts per 100 parts by weight of polymeric material are preferred.

Concentrations of free radical initiators useful in the present invention are from .1 part to 5 parts per 100 parts by weight of polymeric material, but from .5 part to 2 parts per 100 parts by weight of polymeric material are preferred. When using free radical initiation from high energy sources such as Cobalt 60, a level of radiation of 5 to 100 megarads can be used, but from 20 to 50 megarads is preferred.

The blending of the antioxidant and the free radical initiator into the polymer is carried out at a temperature of from 20°C. to 160°C., with a range of from 50°C. to 100°C. being preferred for as long a period of time as is necessary to accomplish the chemical bonding. Time for the bonding reaction to be completed usually ranges from one-half minute to sixty minutes, but from two to ten minutes is usually sufficient.

The present invention includes a process for chemically bonding antioxidants containing aliphatic unsaturation to rubber latex or solution comprising forming a mixture of the antioxidant and the latex or solution in the presence of a free radical initiator, the antioxidant containing aliphatic unsaturation and being an acyclic compound or aryl-substituted acyclic compound. However, in aqueous rubber latex, the reaction time and temperature which are advisable are generally different from those which are advisable in the case of the dry rubber. The invention is also useful for polymers made in organic solution such as hexane and pentane. Examples of such polymers include cis-polyisoprene, cis-polybutadiene, ethylene propylene rubber (EPR) and ethylene/propylene/diene rubber (EPDM). Blending in latex is usually carried out for from 2 hours to 24 hours at a temperature of from 20°C. to 90°C.

Selection of free radical initiators is made based on the method of reaction and the temperatures used. Methods of blending polymers and of adding materials are well known to those skilled in this art. For example, blending on a mill requires that a free radical initiator be used which has a longer half-life than if blending is accomplished using a Banbury internal mixer. Temperature developed during the mixing cycle also determines the type of free radical initiator needed. Curatives and reinforcing agents may be added to the polymeric material after the antioxidant has been chemically bound into the polymeric material.

Practice of the invention is illustrated in the examples below. All parts and percentages are by weight unless otherwise specified. The procedure used for preparing and

testing the polymer samples is illustrated below using natural rubber as a typical polymer.

Natural rubber was milled for five minutes at 55°C. to 60°C. The rubber was sheeted from the mill at approximately .020 inch gauge. Strips were cut from the sheet and extracted with acetone for ten days at room temperature, changing the solvent every other day. Oxygen absorption measurements were made at 90°C. The testing procedure is fully detailed in Industrial and Engineering Chemistry, 43, page 456 (1951) and Industrial and Engineering Chemistry, 45, page 392 (1953).

The antioxidants used are named and described as follows:

(A) N - (4 - anilinophenyl)methacrylamide, whose method of preparation is well known in the art and described in U.S. Patent 3,658,769.

(B) 4 - (3,5 - Di - t - butyl - 4 - hydroxyphenyl)-2-butyl methacrylate was prepared in the following manner.

A two-liter flask was charged with 105 grams (1.05 moles) acetyl acetone, 142 grams (1.025 moles) K₂CO₃, and one liter of ethanol. Over a one hour period 254 grams (1.0 mole) of 3,5-di-t-butyl-4-hydroxy benzyl chloride was added dropwise. A monoalkylated diketone formed, thickening the mixture. The mixture was heated to a vigorous reflux for six hours and then cooled to room temperature. Sodium borohydride, 15 grams (0.4 mole) was added slowly over a 15 minute period. The mixture was stirred at 40°C. for four hours and allowed to stand overnight at room temperature. The mixture was then hydrolyzed with dilute 1:1 concentrated hydrochloric acid and water. Hydrolysis was considered to be complete when gas evolution ceased. Potassium chloride salt was removed from the mixture by filtration and ethanol removed by distillation. The residue was poured into excess cooled water and allowed to stand until crystallization was complete, about 1 to 2 hours. The product was removed from solution and allowed to air dry.

The product, 69.5 grams (.25 mole) was placed in a one liter flask with 350 milliliters of methyl methacrylate, 0.5 gram hydroquinone and 5 grams tetraisopropyl titanate. The mixture was heated to reflux and a methanol-methylmethacrylate azeotrope was removed over a 3½ hour period. The reaction flask was cooled slightly and 20 milliliters water was added dropwise to hydrolyze the catalyst. The reaction mixture was cooled to room temperature and 3 grams sodium carbonate was added. The reaction mixture was stirred for 15 minutes after the addition of sodium carbonate and then filtered. One hundred milliliters of hexane was added to the filtrate forming two phases. The organic phase was removed, dried over magnesium sulfate and the solvent was evaporated to obtain 82 grams (95%) of 4-(3,5-di-t-butyl-4-hydroxyphenyl)-2-butyl methacrylate.

(C) 3 - (3,5 - Di - t - butyl - 4 - hydroxyphenyl)propyl methacrylate was prepared in the following manner.

The preparation was the same as that described for antioxidant (B) except that 66 grams (.25 mole) of 3(3,5-di-t-butyl-4-hydroxyphenyl)propanol was used in place of 69.5 grams (.25 mole) of 4-(3,5-di-t-butyl-4-hydroxyphenyl)-2-butanol.

(D) The reaction product of N-methylmaleimide and p-aminodiphenylamine was prepared in the following fashion. Maleimide (49 grams) was placed in suspension with 40.5 milliliters of 37 percent formalin. A 5 percent aqueous solution of sodium hydroxide (1.5 milliliters) was added to the mixture at 30°C. The mixture cleared in an hour and the product crystallized after standing overnight. The N-methylolmaleimide was filtered and washed with cold ether to yield 49.6 grams of product having a melting point between 95°C. and 98°C.

N-methylolmaleimide (40 grams) was added to 100 milliliters of dioxane in a 500 milliliter flask with stirring and under a nitrogen purge. Distilled p-aminodiphenylamine (58.9 grams) was added and the mixture heated to reflux. The dioxane was removed on a rotary evaporator and the product used without further purification. The product was predominantly N-[(4-anilinophenyl)-aminomethyl]maleimide.

(E) The reaction product of allyl glycidyl ether and p-aminodiphenylamine was prepared in the following manner: p-Aminodiphenylamine (184 grams) and 138 grams of allyl glycidyl ether were placed in a two-liter flask. Isopropanol (800 milliliters) was added and the mixture was refluxed for 8 hours under a slow nitrogen purge. The isopropanol was removed on a rotary evaporator and 316 grams of product was used without further purification. The antioxidant product was predominantly 3-N-(4-anilinophenyl)amino-2-hydroxypropyl allyl ether.

(F) 3,5 - Di - t - butyl - 4 - vinylphenol was prepared in the following manner.

Five grams of 4-ethylidene-2,6-di-t-butylcyclohexa-2,5-dienone, 5 to 10 grams of anhydrous neutral Al₂O₃, and 75 milliliters of petroleum ether were charged into a round bottomed flask. The flask was stirred with a magnetic stirrer while heated to a temperature between 70°C. and 80°C. for 30 to 60 minutes. The mixture was cooled and the petroleum ether removed to yield a residue which was recrystallized from acetone at -78°C. to give 3,5-di-t-butyl-4-vinylphenol in 95 to 100 percent yield.

(G) The reaction product of glycidyl methacrylate and p-aminodiphenylamine was obtained using the following procedure. p-

Aminodiphenylamine (184 grams) and 138 grams of glycidyl methacrylate were placed in a two-liter flask. Isopropanol (800 milliliters) was added and the mixture was refluxed for 8 hours under a slow nitrogen purge. The isopropanol was removed on a rotary evaporator, 316 grams of product being obtained. The product was used without further purification. The antioxidant was predominantly 3 - N - (4' - anilinophenyl)amino - 2-hydroxypropyl methacrylate.

Example 2 shows two parts per 100 parts of the extracted rubber of antioxidant (A)

using the same procedure as described in Example 1. In Examples 3 to 5, two parts per hundred rubber of a free radical initiator, lauroyl peroxide, was added both separately and with triethanolamine and compared to triethanolamine added alone. The test strips were tested for oxygen absorption both before and after extraction in acetone.

Duplicate test strips were heated for an additional 30 minutes at 120°C. in a curing press and again checked with and without being extracted in acetone. The results are shown in Table I.

TABLE I

Example	1	2	3	4	5
Natural rubber	100				
Antioxidant A	0	2			
Triethanolamine			2		
Lauroyl peroxide				2	2
<u>Hours to 1% Oxygen at 90° C.</u>					
As is	229	422	465	695	458
Acetone extracted	9	81	55	243	225
<u>Hours to 1% Oxygen at 90° C. after heating</u>					
As is	216	334	481	555	484
Acetone extracted	9	80	107	245	329

Examples 6—8.

Similar experiments using the same procedure as described in Examples 1 to 5 were carried out in styrene/butadiene rubber using antioxidant (B) as the additive. After test strips were cut from the milled sheet, they were heated in a press for 30 minutes at

120°C. and then extracted for 48 hours in a Soxhlet apparatus with acetone. Oxygen absorption measurements were then made as described in Example 1 except that a temperature of 100°C. was used. The results are given in Table II.

TABLE II

Example	6	7	8
SBR-1502	100		
Antioxidant B	2		
t-Butyl perocetoate	3		
Benzoyl peroxide		3	
Lauroyl peroxide			3
<u>Hours to 1% Oxygen at 100° C.</u>			
Acetone extracted	235	185	280

Examples 9—11.

Further experiments were made in natural rubber using antioxidants of allyl and maleimide derivatives as the additives. Dicumyl peroxide was used as the free radical initiator. The samples were cured for 45 minutes at

150°C. and then extracted with acetone in a Soxhlet apparatus for 48 hours. Oxygen absorption measurements were then made at 90°C. as described in Example 1. The results are shown in Table III.

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TABLE III

Example	9	10	11
Natural rubber	100		→
Dicumyl peroxide	1.25		→
Antioxidant C	2		
Antioxidant D		2	
Antioxidant E			2

Hours to 1% Oxygen at 90°C.

Acetone extracted	528	380	365
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Examples 12—16.

Additional experiments were made in natural rubber using dicumyl peroxide as the free radical initiator which tested various additives including vinyl compounds such as

antioxidant (F). The procedure in all tests was the same as was used to produce the results in Table III. The results are shown in Table IV.

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TABLE IV

Example	12	13	14	15	16
Natural rubber	100				
Dicumyl peroxide	0.5				→
Antioxidant F		2			→
Antioxidant C			2		
Antioxidant G				2	
Antioxidant A					2

Hours to 1% Oxygen at 90°C.

Acetone extracted	10	275	505	550	250
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The examples given in the above tables show several antioxidants built into the polymer using the process of this invention. These antioxidants give protection to the extracted vulcanizates particularly when a peroxide such as dicumyl peroxide is used as a curative.

In Examples 17 through 20, dicumyl peroxide was used as the free radical initiator

in ethylene/propylene/diene (EPDM) and ethylene/propylene (EPR) rubbers. The samples were cured for 45 minutes at 150°C. and then extracted with acetone in a Soxhlet apparatus for 48 hours. Oxygen absorption measurements were then made as described in Example 1 except that 120°C. was used.

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TABLE V

Example	17	18	19	20
EPR	100	→		
EPDM			100	→
HAF Black	50			→
Processing oil	10			→
Dicumyl peroxide	2.5		1.5	→
Antioxidant A				1.5

Hours to 1% Oxygen at 120°C.

Acetone extracted	164	186	189	260
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Examples 21—25 show the effect of varying the rubber while using the same antioxidant. The results are shown in Table VII.

TABLE VII

Example	21	22	23	24	25
Antioxidant G	2				→
Natural rubber	100				
Polyisoprene		100			
Styrene/Butadiene			100		
Acrylonitrile/Butadiene				100	
Polychloroprene					100
Lauroyl peroxide	1				→
<u>Hours to 1% Oxygen at 100° C., Unextracted</u>					
	180	291	113	145	27
<u>Hours to 1% Oxygen at 100° C., Acetone Extracted</u>					
	93	122	95	147	52

WHAT WE CLAIM IS:—

1. A process for chemically bonding antioxidants containing aliphatic unsaturation to polymeric materials which comprises heating and reacting a mixture of the polymeric material and antioxidant containing aliphatic unsaturation, in the presence of a free radical initiator, for a time sufficient to cause the antioxidant to chemically bond to the polymer, the antioxidant being an acyclic compound or aryl-substituted acyclic compound. 45

5. A process as described in claim 1 wherein the antioxidant is selected from the group consisting of: N-(4-anilinophenyl)methacrylamide; 4-(3,5-di-t-butyl-4-hydroxyphenyl)-2-butyl methacrylate; 3-(3,5-di-t-butyl-4-hydroxyphenyl)propyl methacrylate; the reaction product of allyl glycidyl ether and p-aminodiphenylamine containing 3-N-(4-anilinophenyl)-amino-2-hydroxypropyl allyl ether; the reaction product of N-methylolmaleimide and p-aminodiphenylamine containing N-[4-anilinophenyl]aminomethyl]maleimide; the reaction product of glycidyl methacrylate and p-aminodiphenylamine containing 3-N-(4-anilinophenyl)amino-2-hydroxypropyl methacrylate; and 3,5-di-t-butyl-4-vinylphenol. 50

10. A process as described in claim 1 wherein the radical initiator is selected from the group consisting of peroxides and high energy radiation. 55

15. A process as described in claim 2 wherein the free radical initiator is a peroxide selected from the group consisting of lauroyl peroxide, benzoyl peroxide, dicumyl peroxide, di-t-butyl peroxide, 2,5-dimethyl-2,5-bis(2-ethylhexanoylperoxy)hexane, acetyl peroxide, t-butyl peroxydicarbonate, t-butyl peracetate, t-butyl peroxyvalate, t-butyl perbenzoate, t-butyl peroxytoate, 2,4-dichlorobenzoyl peroxide, 1,1-bis(t-butyldperoxy)-3,3,5-trimethylcyclohexane, α,α' -bis(t-butyldperoxy)diisopropylbenzene, 2,5-dimethyl-2,5-di(t-butyldperoxy)hexane, di(sec-butyl) peroxydicarbonate, diisopropyl peroxydicarbonate, t-butyl peroxyvalate, t-butyl peroxyisobutyrate, t-butyl peracetate, 1,1,3,3-tetramethylbutyl peroxy-2-ethyl hexanoate, t-butylperoxy isopropyl carbonate, acetyl cyclohexylsulfonyl peroxide, t-butylperoxyisopropyl carbonate, t-butyl hydroperoxide, 2,5-dimethyl-2,5-di(hydroperoxy)hexane, cumene hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, isopropylbenzene dihydroperoxide, p-menthane dihydroperoxide and t-butyl dihydroperoxide. 60

20. A process as described in claim 2 wherein the free radical initiator is a peroxide selected from the group consisting of lauroyl peroxide, benzoyl peroxide, dicumyl peroxide, di-t-butyl peroxide, 2,5-dimethyl-2,5-bis(2-ethylhexanoylperoxy)hexane, acetyl peroxide, t-butyl peroxydicarbonate, t-butyl peracetate, t-butyl peroxyvalate, t-butyl perbenzoate, t-butyl peroxytoate, 2,4-dichlorobenzoyl peroxide, 1,1-bis(t-butyldperoxy)-3,3,5-trimethylcyclohexane, α,α' -bis(t-butyldperoxy)diisopropylbenzene, 2,5-dimethyl-2,5-di(t-butyldperoxy)hexane, di(sec-butyl) peroxydicarbonate, diisopropyl peroxydicarbonate, t-butyl peroxyvalate, t-butyl peroxyisobutyrate, t-butyl peracetate, 1,1,3,3-tetramethylbutyl peroxy-2-ethyl hexanoate, t-butylperoxy isopropyl carbonate, acetyl cyclohexylsulfonyl peroxide, t-butylperoxyisopropyl carbonate, t-butyl hydroperoxide, 2,5-dimethyl-2,5-di(hydroperoxy)hexane, cumene hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, isopropylbenzene dihydroperoxide, p-menthane dihydroperoxide and t-butyl dihydroperoxide. 65

25. A process as described in claim 4 wherein the chemical bonding is carried out at a temperature of from 20°C. to 160°C. 70

30. A process as described in claim 4 wherein the chemical bonding is carried out for from 0.5 minutes to 60 minutes. 75

35. A method as described in claim 1 wherein curatives and reinforcing agents are added to the polymeric material after the antioxidant has been chemically bound into the polymeric material. 80

40. A process for chemically bonding antioxidants containing aliphatic unsaturation to rubber latex or solution comprising forming a mixture of the antioxidant and the latex or solution in the presence of a free radical initiator, the antioxidant containing aliphatic unsaturation and being an acyclic compound or aryl-substituted acyclic compound. 85

4. A process as described in claim 1 wherein the polymeric material is a rubber selected from the group consisting of natural rubber,

the group consisting of peroxides and high energy radiation.

11. A process as described in claim 10 wherein the free radical initiator is a peroxide selected from the group consisting of lauroyl peroxide, benzoyl peroxide, dicumyl peroxide, di-t-butyl peroxide, 2,5-dimethyl-2,5-bis(2-ethylhexanoylperoxy)hexane, acetyl peroxide, t-butyl peroxymaleic acid, t-butyl peracetate, t-butyl peroxyvivate, t-butyl perbenzoate, t-butyl peroctoate, 2,4-dichlorobenzoyl peroxide, 1,1 - bis(t - butylperoxy) - 3,3,5 - trimethylcyclohexane, α,α' - bis(t - butylperoxy)diisopropylbenzene, 2,5 - dimethyl - 2,5 - di(t - butylperoxy)hexane, di(sec - butyl) peroxydicarbonate, diisopropyl peroxydicarbonate, t-butyl peroxyvivate, t-butyl peroxyisobutyrate, t-butyl-peracetate, 1,1,3,3-tetramethylbutyl peroxy-2-ethyl hexanoate, t-butyl peroxy isopropyl carbonate, acetyl cyclohexylsulfonyl peroxide, t-butylperoxyisopropyl carbonate, t-butyl hydroperoxide, 2,5-dimethyl-2,5 - di(hydroperoxy)hexane, cumene hydroperoxide, 1,1,3,3 - tetramethylbutyl hydroperoxide, isopropylbenzene dihydroperoxide, p-methane dihydroperoxide and t-butyl dihydroperoxide.

12. A process as described in claim 9 wherein the polymeric material is a rubber latex or solution selected from the group consisting of natural rubber, cis-polyisoprene rubber, polybutadiene rubber, styrene/butadiene rubber, acrylonitrile/butadiene rubber, ethylene/propylene rubber and ethylene/propylene/diene rubber.

13. A process as described in claim 9 wherein the antioxidant is selected from the group consisting of: N-(4-anilinophenyl)-methacrylamide; 4 - (3,5 - di - t - butyl - 4-hydroxyphenyl) - 2 - butyl methacrylate; 3 - (3,5 - di - t - butyl - 4 - hydroxyphenyl) - propyl methacrylate; the reaction product of allyl glycidyl ether and p-aminodiphenylamine containing 3 - N - (4 - anilinophenyl)amino - 2 - hydroxypropyl allyl ether; the reaction product of N-methylolmaleimide and p-aminodiphenylamine containing N - [(4 - anilinophenyl)amino-methyl]maleimide; the reaction product of glycidyl methacrylate and p-aminodiphenylamine containing 3 - N - (4' - anilinophenyl)amino - 2 - hydroxypropyl methacrylate; and 3,5-di-t-butyl-4-vinylphenol.

14. A process as described in claim 9 wherein the chemical bonding is carried out at a temperature of from 20°C. to 90°C.

15. A process as described in claim 9 wherein the chemical bonding is carried out for from 2 hours to 24 hours.

16. A method as described in claim 9 wherein curatives and reinforcing agents are added to the polymeric material after the antioxidant has been chemically bound into the polymeric material.

17. Polymeric materials containing bound antioxidants when produced by the process of this invention.

18. Articles containing polymeric materials having bound antioxidants produced by the process of this invention.

19. A process as described in claim 1 or 9, wherein the procedure is substantially as indicated in respect of any of the foregoing Examples.

20. Polymeric materials containing bound antioxidants when produced by the process of claim 19.

21. Articles containing polymeric materials having bound antioxidants produced by the process of claim 19.

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